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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Ted TSAI

Application No.: 09/609,513

Filing Date: July 3, 2000

Title: MINIMIZING CHLORINATED ORGANICS IN PULP BLEACHING PROCESSES

Examiner: M. Alvo

Group Art Unit: 1731

DECLARATION OF TED Y. TSAI UNDER 37 C.F.R. §1.131

Honorable Commissioner for Patents
Washington, D.C. 20231

MPEP 715

Sir:

I, Ted Y. Tsai, declare that:

1. I am the inventor of the subject matter of the above-referenced invention, and I am an employee of the assignee of the application, International Paper Company.

2. I am intimately familiar with the application and the history of conception and reduction to practice of the invention described and claimed in the application.

3. Long before October 1, 1995, I observed that hydrogen peroxide was useful for the bleaching of pulps produced pulps having high brightness values and that the amount of halogenated waste products was significantly reduced as compared to traditional bleaching sequences employing only chlorine and / or chlorine dioxide along with alkaline extraction. However, peroxide bleached typically exhibited significant reductions in pulp viscosity and yield as compared to the traditional bleached pulps of comparable brightness.

4. I suggested that research be carried out with the aim of reducing the negative effects of peroxide bleaching on pulp viscosity and yield while retaining the high brightness levels and low halogenated waste product levels associated with peroxide bleaching. I conceived that this may be achievable via specific bleaching stages employing

one or more initial chlorine dioxide stages, a final peroxide stage, and certain additives which protect the viscosity and yield properties of the pulp.

5. To that end, an investigation was conducted of different bleaching sequences and additives. From the investigation, I determined that pulp could advantageously be bleached in a sequence having a first chlorine dioxide stage, a second chlorine dioxide stage, and a final peroxide stage with a chelating agent additive being added to the pulp prior to the final peroxide stage. I found that such a bleaching sequence produced pulps having excellent brightness values while preserving viscosity and pulp yield values comparable to non-peroxide based bleaching sequences.

6. Conception and reduction to practice of my invention is evidenced in the attached Record of Invention Memorandum (Exhibit A) I prepared and sent to International Paper's patent counsel well before October 1, 1995. All of the experiments described in the Memorandum were carried out well before October 1, 1995. As may be seen from the Tables on pages 4 - 13 of the Memorandum, I carried out numerous experiments wherein a pulp was bleached in a $D_oE_{o+p}DP$ (which may also be characterized as a D_1, $E_{o+p}D_2P$ sequence) bleaching sequence in which a chelating agent such as EDTA or DTPA was added to the second "D" stage (Examples 2 - 8, 12 - 18). The experiments revealed favorable results both in terms of viscosity and yield and in terms of final brightness values.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: October 17, 2001

Ted Tsai

Ted Y. Tsai

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[redacted] TERNAL MEMORANDUM RECEIVED

INTERNATIONAL PAPER
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-- CONFIDENTIAL --

February

SUBJECT: IP Case 4779; Bleaching Processes for Minimizing Chlorinated Organics

TO: P. Hodges
W.T. Zielinski

FROM: T.Y. Tsai

cc: T.E. Amidon
R.B. Phillips (Bel Air)
J.J. Renard (Bel Air)
Central Files (0806-00)

Attached please find the results from our recent study for IP Case 4779: Bleaching Processes for Minimizing Chlorinated Organics. It focuses on:

* The effect of changing T stage in a bleaching sequences,
* The effect of different CAs,
* The sequential and simultaneous addition of CAs,
* The use of CA in a bleaching tower dilution or washer vat,
* The use of CA in an extraction stage.

If you have any questions, please call me at (914) 577-7471. Thank you very much.

Ted Tsai
T.Y. Tsai

jm[24779.tt]
Att.

EXHIBIT
TAGGED
A

IP Case 4779: Bleaching Processes for Minimizing Chlorinated Organics

[1] Prior Art:

In order to reduce the formation of dioxin and chlorinated organics, the use of chlorine-compounds can be decreased by increasing temperature, pressure, or chemical charge in Eo+p or E2 stage. But, the amount of peroxide can be used is low because of pulp viscosity and yield loss.

[2] Objective of this Invention:

The object of this invention is to use chelating agents (CAs) in a chlorine, chlorine dioxide, or alkaline stage or a combination of stages to improve the efficiency of non-chlorine-compound bleaching, especially peroxide, and reduce the use of chlorine-compounds with reduced loss of pulp viscosity and yield compared to current technology. Some operating windows for technical success have been identified.

[3] Technical Findings:

The following nine points summarize the important findings:

(1) The CA can boost pulp brightness in the peroxide stage, particularly in a P stage after a chlorine dioxide stage. The addition of CA can prevent viscosity loss up to a certain brightness above which the protecting effect decreases and the brightness level at which the change occurs depends on the characteristics of pulp that have not been fully explored.

(2) The screening of 7 CAs indicated that EDTA and DTPA are the most effective chemicals (Exp No. 1-8 and 11-18).

(3) The sequential addition of CA is more efficient than simultaneous addition with chlorine dioxide or chlorine or a mixture (Exp No. 1-8, 11-18 and previous ROI). We expect that the application of hypochlorous acid follows the same rule.

(4) CA can be added in the washer vat or bleaching tower exit dilution zone (Exp No. 21-28).

(5) The addition of CA can be in chlorination or chlorine dioxide stage or the combination (discussed in previous ROI).

(6) T stages (addition of CA) can be added in different places of a bleaching sequence, but the addition of CA in a D1 or after a D1 stage is more efficient than other placements tested (an important finding, Exp No 31-36).

(7) The addition of CA can be in an extraction stage or the combination of chlorination and extraction stages (Exp No 41 to 48).

(8) CA can be applied in 3 [D/CEo+pP], 3-1/2 [D/CEo+p(dP) or D/CEo+p(hP)], 4 [D/CEo+pDP], 5 [D/CEo+pDPD], or 6 [OD/CEo+pDPD] stage bleaching sequences.

(9) CA can be used in chlorine, chlorine-free, and chlorine-compound-free bleaching processes.

[4] EXAMPLES

ABBREVIATIONS FOR TABLES

TEA: Triethanolamine
GA: Gluconic acid
STP: Sodium triphosphate
TAR: Sodium tartrate
DMA: 2-hydroxy-4,6,-dimethoxy-acetophenone
DTPMA: Diethylene-triamine-penta-methylene-phosphonic acid CA or
EDTA: Disodium salts of ethylene-diamine-tetra-acetic acid
DTPA: Penta-sodium salts of diethylene-triamine-pentaacetic acid
CS: Sandoz stabilizer CS

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Explanation for Table 1:

Different CAs are added in the chlorine dioxide stage of DoEo+pDP sequence after chlorine dioxide (D) is added. The time can range from a few seconds to 1 to 2 hrs. The addition of CAs results in an increase in the efficiency of subsequent peroxide stage bleaching. Approximately 1 to 2.5 units higher brightness are obtained. With EDTA and CZ (Exp No 2 and 8), the final pulp viscosity is 1 to 3.5 point higher than the control.

Table 1 - The Effect of Sequential Addition of CA in D1 Stage

Exp No	Bleaching Sequences	CA in D Stage	Brightness (%GE)	Viscosity (cP)
1	DoEo+pDP	No CA (Control)	86.3	15.7
2	DoEo+pDP	0.4% EDTA after 30 min	88.7	19.5
3	DoEo+pDP	0.2% DTPA after 30 min	88.9	15.1
4	DoEo+pDP	0.5% STP after 30 min	87.1	11.6
5	DoEo+pDP	0.3% DTPMA after 30 min	88.3	13.8
6	DoEo+pDP	0.3% DMA after 30 min	87.5	15.1
7	DoEo+pDP	0.5% TAR after 30 min	87.5	11.3
8	DoEo+pDP	1% CZ after 30 min	87.3	16.8

Notes:

(1) Pine Bluff softwood pulp, Kappa=30.7, viscosity =31.7 cP
(2) Bleaching Conditions:
Do stage: 0.2 chlorination factor, 50°C, 40 min., 10% csc.
Eo+p stage: 2.7% NaOH, 0.6% peroxide, 10% csc, 1 hr., 85°C.
D stage: 0.4% chlorine dioxide, 0.16% NaOH, 10% csc, 90°C, 1.5 hrs.
P stage: 1.5% peroxide, 1% NaOH, 0.05% MgSO4, 90°C, 10% csc, 3 hrs.

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Explanation for Table 2:

The addition of CAs with chlorine dioxide in the chlorine dioxide stage (D) of a DoEo+pDP sequence produced a small brightness

gain in Exp No 12 and 18 and a 3.8 point viscosity gain in Exp No 12.

Table 2 - The Effect of Simultaneous Addition of CA in D1 Stage

Exp No	Bleaching Sequences	CA in D Stage	Brightness (%GE)	Viscosity (cP)
11	DoEo+pDP	No CA	87.3	15.3
12	DoEo+pDP	0.4% EDTA	87.5	19.5
13	DoEo+pDP	0.2% DTPA	85.0	17.2
14	DoEo+pDP	0.5% STP	86.8	12.8
15	DoEo+pDP	0.3% DTPMA	86.5	13.6
16	DoEo+pDP	0.3% DMA	85.0	14.5
17	DoEo+pDP	0.5% TAR	87.2	14.6
18	DoEo+pDP	1% CZ	87.8	12.7

Notes:

(1) Pine Bluff softwood pulp, Kappa=30.7, viscosity=31.7 cP
(2) Bleaching Conditions:
Do stage: 0.2 chlorination factor, 50°C, 40 min., 10% csc.
Eo+p stage: 2.7% NaOH, 0.6% peroxide, 10% csc, 1 hr., 85°C.
D stage: 0.4% chlorine dioxide, 0.16% NaOH, 10% csc, 90°C, 1.5 hrs.
P stage: 1.5% peroxide, 1% NaOH, 0.05% MgSO4, 90°C, 10% csc, 3 hrs.

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Explanation of Table 3:

In Table 3, the CAs are added at the end of D stage bleaching to simulate addition in the bleaching tower dilution zone or washer vat dilution zone. Compared to Exp No 11 (control, 87.3 %GE brightness), the addition of CAs improves the brightness by about 1 to 2.5 point.

Table 3 - The Effect of CA Addition in DI Dilution Zone or Washer Vat

Exp No	Bleaching Sequences	CA in D Stage washer vat	Brightness (%GE)	Viscosity (cP)
11	DoEo+pDP	No CA	87.3	15.3
21	DoEo+pDP	0.4% EDTA	88.9	17.9
22	DoEo+pDP	0.2% DTPA	89.4	13.8
23	DoEo+pDP	0.5% STP	89.8	14.6
24	DoEo+pDP	0.3% DTPMA	88.3	16.0

Notes:

(1) Pine Bluff softwood pulp, Kappa=30.7, viscosity=31.7 cP
(2) Bleaching Conditions:

Do stage: 0.2 chlorination factor, 50°C, 40 min., 10% csc.
Eo+p stage: 2.7% NaOH, 0.6% peroxide, 10% csc, 1 hr., 85°C.
D stage: 0.4% chlorine dioxide, 0.16% NaOH, 10% csc, 90°C, 1.5 hrs. The CAs were added at the end of bleaching, dissolved CA in 60°C and pH 4 water, and mix for 1 min.
P stage: 1.5% peroxide, 1% NaOH, 0.05% MgSO4, 90°C, 10% csc, 3 hrs.

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Explanation for Table 4:

This table (Table 4) designed to compare the effect of acidic washing (with and without CA) on the enhancement of peroxide bleaching. The CA is added three ways for comparison 5 minutes later after chlorine dioxide addition (Exp No 26), or at the dilution zone (Exp No 28), at the washer vat (Exp No 27). All three options show a 2 to 3 point higher brightness than the acid wash only control (Exp No 25) and 4 to 7 point higher viscosity.

Table 4 - Comparison of Different Modes of CA Addition

Exp No	Bleaching Sequences	CA in D Stage	Brightness (%GE)	Viscosity (cP)
25	DoEo+pDP	No CA Only acid wash (60 C)	86.8	9.8
26	DoEo+pDP	0.4% EDTA added After 5 min Acid wash (60 C)	89.8	16.8
27	DoEo+pDP	0.4% EDTA added to acidic washing liquor (60 C) 1% csc	88.7	13.4
28	DoEo+pDP	0.4% EDTA added at end, 10% csc then diluted to 1% csc (60 C)	89.5	13.3

Notes:

(1) Pine Bluff softwood pulp, Kappa=30.7, viscosity=31.7 cP
(2) Bleaching Conditions:
Do stage: 0.2 chlorination factor, 50°C, 40 min., 10% csc.
Eo+p stage: 2.7% NaOH, 0.6% peroxide, 10% csc, 1 hr., 85°C.
D stage: 0.4% chlorine dioxide, 0.16% NaOH, 10% csc, 90°C, 1.5 hrs. The CAs were added at the end of bleaching, dissolved CA in 60°C and pH 4 water, and mix for 1 min.
P stage: 1.5% peroxide, 1% NaOH, 0.05% MgSO4, 90°C, 10% csc, 3 hrs.

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Explanation to Table 5:

This experiment is to compare the effect of inserting a T stage in different stage of a bleaching sequence.

The following 6 options are studied:

* T is added before extraction stage with washing after chlorination stage (Exp No 31), or
* T is before extraction stage without washing after chlorination stage (Exp No 32), or
* T after extraction stage but before D stage (Exp No 33), or

* CA is added in D stage after chlorine dioxide is added (Exp No 34), or
* CA is added in the D stage washer vat (Exp No 35), or D is after T but before P stage (Exp No 36).

The results show that about 1 to 2.5 points brightness gain. Both the addition of CA after the addition of chlorine dioxide in D stage (Exp No 35) and T stage after D stage produce 2 to 3 point higher brightness. It indicates that to insert T stage in a later stage is more effective.

Table 5 - Comparison of Effect of Changing T Stage in a Bleaching Sequence

Exp No	Bleaching Sequences	CA Conditions	Brightness (%GE)	Viscosity (cP)
1	DoEo+pDP	No CA (Control)	86.3	15.7
31	DoTEo+pDP	As Note (2)	87.3	12.6
32	(DoT)Eo+pDP	As Note (2)	87.3	11.4
33	DoEo+pTDP	Separate T stage	88.9	12.3
34	DoEo+p(D->T)P	Add 0.4% EDTA After 5 min	88.8	18.6
35	DoEo+p(Dt)P	Add to washer vat	86.7	15.6
36	DoEo+pDTP	Separate T stage	88.9	17.9

Notes:

(1) Pine Bluff softwood pulp, Kappa=30.7, viscosity=31.7 cP
(2) Bleaching conditions:
Do stage: 0.2 chlorination factor, 50°C, 40 minutes, 10%csc.
T stage: Before Eo+p stage, 0.4% EDTA, 50°C, 40 mim., pH=1.6.
Eo+p stage: 2.7% NaOH, 0.6% peroxide, 85°C, 1 hr, 10%csc, oxygen pressure from 45 psig to 0 psig within 1 hr.
D stage: 0.4% chlorine dioxide, 0.16% NaOH, 1.5 hrs, 10% csc, 70°C, acid wash with about pH 4 water. CA is disodium salt of EDTA.
T stage: After Eo+p stage, pH=4, 90°C, 10% csc, 1 hr.
P stage: 1.5% peroxide, 1% NaOH, 0.05% MgSO4, 90°C, 3 hrs, 10% csc.

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Explanation for Table 6:

In this experiment, CAs are added in extraction stage and D1 stage to explore the possibility of using CAs in extraction stage.

For a DoEpP sequence, Exp No 41 has no any CA in any stages. Exp No 42 has TEA in extraction stage, and Exp No 43 has GA and MgSO4 in extraction stage. With GA a 7 point higher brightness is obtained (78.0 vs 70.9 %GE), while with TEA, a 2.3 point brightness gain is resulted (73.2 vs 70.9 %GE).

For DoEpDP sequence, while CA can be added in D stage to evaluate the effect of CA in extraction stage.

(1) For no CA in extraction stage, as previous results showed that adding CA in D stage (Exp 41d vs 41b) has a 4 point brightness gain (87.6 vs 83.2 %GE).

(2) For adding TEA in extraction stage, same as above results, only 4 point brightness gain is obtained. That means even though TEA remove some harmful metals from the pulp. But its effect is less than that adding CA in D stage.

(3) For adding GA and MgSO4 in extraction stage, the addition of CA in D stage only show slightly brightness gain (Exp No 43d vs 43b), but some viscosity loss. Without CA in the D stage, similar to that with CA 87.1 %GE brightness is obtained. However, high pulp viscosity is obtained (22.2 cP vs 12.9 cp).

Table 6 - Effect of CA in Extraction and D1 Stages

Exp No	Bleaching Sequences	Ep Stage	D Stage	Brightness (%GE)	Viscosity (cP)
41	DoEpP	No additive	No	70.9	23.3
41a	DoEpD	Same as above	Acid wash (pH=4)	77.2	25.2
41b	DoEpDP	Same as above	Acid wash (pH=4)	83.2	16.4
41c	DoEpD	Same as above	Add CA after 30 min.	77.3	28.7
41d	DoEpDP	Same as above	Add CA after 30 min.	87.6	16.2
42	DoEpP	0.9% TEA	No	73.2	25.9
42a	DoEpD	Same as above	Acid wash (pH=4)	77.2	27.2
42b	DoEpDP	Same as above	Acid wash (pH=4)	83.2	16.8
42c	DoEpD	Same as above	Add CA after 30 min.	77.5	26.8
42d	DoEpDP	Same as above	Add CA after 30 min.	87.7	16.0
43	DoEpP	1.4% GA 0.4% MgSO4	No	79.1	21.3
43a	DoEpD	Same as above	Acid wash (pH=4)	78.0	30.6
43b	DoEpDP	Same as above	Acid wash (pH=4)	87.1	22.2
43c	DoEpD	Same as above	Add CA after 30 min.	79.4	28.6
43d	DoEpDP	Same as above	Add CA after 30 min.	87.8	12.9

Notes:

(1) Pine Bluff softwood pulp, Kappa=30, viscosity=31.7 cP
(2) Bleaching conditions:
Do stage: 0.2 chlorination factor, 50°C, 40 minutes, 10%csc.
Ep stage: 2.7% NaOH, 1% peroxide, 90°C, 1 hr, 10%csc. TEA is triethanolamine, GA is potasium salt of D-Gluconic acid. The brightness of Ep pulp for Exp 41; 58.3, Exp 42; 66.1, Exp 43; 62.5 %GE.
D stage: 0.4% chlorine dioxide, 0.16% NaOH, 1.5 hrs, 10% csc, 70°C, acid wash with about pH 4 water. CA is disodium salt of EDTA.
P stage: 2% peroxide, 1.3% NaOH, 0.05% MgSO4, 90°C, 3 hrs, 10% csc.

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Explanation for Table 7:

Table 7 illustrates the results of adding CA in the extraction stage only. With or without a T stage, Exp No 47 and 47a or Exp 48 and 48a produce same brightness. This indicates that the addition of CA in the extraction stage produces similar effect as that T after extraction stage.

Table 7 - Effect of CA in Extraction Stage Only

Exp No	Bleaching Sequences	Ep Stage	P Stage	Brightness (%GE)	Viscosity (cP)
47	DoEpTP	No P	0.81%P com	75.6	26.1
47a	DoEpP	No P	1.35%P com	75.6	21.0
48	DoEpTP	2% P	0.82%P com	81.0	21.5
48a	DoEpP	2% P	0.74%P com	81.1	22.1

Notes:

(1) Pine Bluff softwood pulp, Kappa=30.7, viscosity=31.7 cP
(2) Bleaching conditions:
Do stage: 0.2 chlorination factor, 50°C, 40 minutes, 10% csc,
Ep stage: 4% Na2CO3, 90°C, 1 hr, 10% csc. DTPA is pentasodium DTPA.
The brightness of Ep pulp for Exp 47; 35.7,
Exp 48; 62.2 %GE.
T stage: 0.4% CA, pH=4-5, 10% csc, 90°C, 1 hr.
P stage: 2% peroxide, 1.3% NaOH, 0.05% MgSO4, 90°C, 3 hrs,
10% csc.

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Explanation of Table 8:

Table 8 illustrates the application of this invention on hardwood pulp. This invention provided 4-10 points (Exp No 114a, 116, 117) higher brightness than the conventional process (Exp No 115a).

Table 8 - Hardwood Pulp Bleaching Study

Exp No	Bleaching Sequences	Do Stage	D1 or P Stage	D2 or P Stage	Brightness (%GE)	Viscosity (cP)
114a	DoEo+pDP	CF=0.2	0.3% D 0.5% CA	0.8% P (0.44% com)	89.1 (87.7)	13.1
115a	DoEo+pDP	CF=0.2	0.3% D No CA	0.8% P	79.5 (77.8)	9.2
116	DoEo+p(DP)	CF=0.2 0.5% CA	0.3% D	0.8% P	86.3 (85.6)	15.5
117	DoEo+p(hP)	CF=0.2 0.5% CA	0.5% h	0.8% P	83.7 (82.8)	13.0

Notes:

(1) Texarkana hardwood pulp, Kappa=14.6, viscosity=22.5 cP
(2) Bleaching conditions:

Do stage: 60°C, 35 minutes, 3.5% csc.
Eo+p stage: 1.5% NaOH, 0.6% peroxide, 85°C, 1hr.
oxygen; 45 psig->0 psig.
D1 stage: 0.4% NaOH factor, 10% csc, 70°C,
1.5 hrs. CA is disodium salt of EDTA.
D2 stage: 10% csc, 70°C, 3 hrs.
P stage: 1.5% NaOH, 0.05% MgSO4, 90°C, 3 hrs, 10% csc.